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The Nature of Thorium in Bauxite and Bauxite Residue from Greece

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Rare earth elements (REEs) are considered strategic metals as they are incorporated in a wide range of materials (e.g., permanent magnets, metal alloys and catalysts) that constitute the often unnoticed matrix of daily-life applications today (e.g., high-efficiency turbines, electric motors in cars and mobile phones).^{e.g.1,2} This has led to a growing demand from high-tech industries and REEs supply risk,³ in view of China's REE export restrictions⁴ regardless its recent plans to eliminate export quota for REEs,⁵ has propelled research towards the use of alternative resources. Bauxite residue (BR), originating from the refining of alumina ore (bauxite) to alumina through the Bayer process, has been identified as a promising source. In this case, REEs and Sc, are of particular interest, and efforts to develop an extraction process also have to provide a clear and safe management strategy for the accompanying actinides, as well. In particular, the environmental significance is critically arising due to the co-existence of Th together with REEs in bauxite and BR.^{e.g.6-8} However, the exact nature of Th in them has been unknown until the recent studies,⁶⁻⁸ constituting the basis of this abstract. Thus, it is crucial to determine Th hosting phases in order to try to separate them, creating a "clean" stream for subsequent REE extraction. To meet this need, we applied electron microscopy (TEM) and synchrotron-based spectroscopy (EXAFS) to understand the nature of Th in the Greek bauxite and BR.⁶⁻⁸ Th in bauxite has been found to be hosted in LREE-minerals (mostly bastnäsite/parisite-group), zircon (ZrSiO_4) and, especially, in anatase (TiO_2) in microscale. The Th L_{III} -edge EXAFS spectra gave evidences that Th^{4+} may not replace Ti^{4+} in distorted $[\text{TiO}_6]$ octahedral units of anatase lattice (CN=6). The occupation of either extraframework sites of higher coordination (CN=6.9 or even CN=7.4) or defected/vacant (\square) sites is more probable.^{6,7} On the other hand, TEM study of BR revealed that Th^{4+} is hosted into a novel perovskite-type phase with major composition $\text{Ca}_{0.8}\text{Na}_{0.2}\text{TiO}_3$. The Th L_{III} -edge EXAFS spectra demonstrated that Th^{4+} ions, which are hosted in the nano-perovskite, occupy Ca^{2+} sites, rather than Ti^{4+} sites.^{7,8} We consider that the study of Th, in bauxite and BR, can redound to a sustainable supply of strategic metals and oxides, contributing to a more sustainable "modus operandi".

[1] Hatch G. P., Elements 8 (2012), 341; [2] <http://www.cnet.com/news/digging-for-rare-earths-the-mines-where-iphones-are-born/>; [3] <http://www.bgs.ac.uk/downloads/start.cfm?id=2643>; [4] <http://investorintel.com/rare-earth-intel/chinas-rare-earth-exports-tumble-january/>; [5] <http://investingnews.com/daily/resource-investing/critical-metals-investing/rare-earth-investing/china-eliminate-rare-earth-export-tariffs-medallion-resources/>; [6] Gamaletsos P. et al., Nucl. Instrum. Meth. B 269 (2011), 3067; [7] Gamaletsos P., PhD Thesis, University of Athens, Greece (2014), 386 pp.; [8] Gamaletsos P. et al., Sci. Rep. (2015 – Under Review)